PCDD/Fs in Ambient Air in Korea : Gas/Particle Partitioning and Relationship with Sources.

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Introduction

Recently, studies about PCDD/Fs have been widely conducted in Korea. However, most of these studies are about incinerators and analysis methods.[1,2] Therefore, there is a considerable lack of data on the levels of PCDD/Fs in the atmospheric environment. PCDD/Fs produced from various sources are emitted into the atmosphere and then transported great distances before being deposited to other environmental compartments. A key process determining the environmetal fate of PCDD/Fs in the atmosphere is their partitioning between particles and gas phase.[3,4] Also, the only pathway to the sinks from combustion sources is through the atmosphere, and so it is very important to verify PCDD/Fs levels in air.

In this paper, measurements of the gas/particle partitioning of PCDD/Fs are presented. PCDD/Fs congener profiles in ambient air and that of sources are compared by PCA analysis.

Experiments

Sampling Sites ; Air samples are taken seasonally from August 1999 to Spring 2000 at three locations in Korea. Their specific locations are as follows, (a) site A ; incineration area within 300 m distance of municipal solid waste incinerator. (b) site B ; industrial area of steel industry. (c) site C ; industrial area of chemical and oil refinary industries.

Sample Collection ; Ambient air samples were collected using a high volume air sampler. A glass fiber filter and polyurethane foam plugs were used to collect airborne particles as well as vapor-phase PCDD/Fs. Before sampling, the filter was baked at 450°C for 12 hours and PUF was pre-cleaned with methylene chloride in soxhlet. Sampling times and air volumes were not much different ; 24 hr , 1000-1300m^3.

Sample preparation ; Sample preparation was done according to the US EPA method 1613. The glass filter and PUF samples were transferred to the glass thimble of the Soxhlet, separately, and spiked with a mixture of $^{13}C_{12}$-labelled PCDD/Fs internal standards (1 ng) and extracted for 16 h with toluene. The extracted samples were washed with H_2SO_4 until colorless and then with hexane rinsed water to make neutralized. Sample cleanup was done in two stages; (a) silica gel column (with layers of basic, neutral, acidic and neutral silica); (b) activated acidic alumina column capped with anhydrous Na_2SO_4, and concentrated with N_2 gas.

PCDD/Fs were analyzed by high-resolution gas chromatography / high-resolution mass spectrometry (Hewlett-Packard Model 6890 serious _/ JMS 700T) wirh a DB-5MS column. The MS was operated at 10,000 resolution under positive EI conditions (38 eV electron energy), and data were obtained in the single ion monitoring (SIR) mode.

Results and Discussion

PCDD/Fs levels in ambient air ; The PCDD/Fs air concentrations measured in this study ranged from 71 fg-TEQ/Nm^3 to 1161 fg-TEQ/Nm^3 and summarized in Table 1. The PCDD/Fs levels of air near incinerator is higher than those of industrial area. Many factors have an influenced PCDD/Fs levels near incinrator area. This sampling site is surrounded by many small factories, including a small incinerator which burns industrial wastes. It was reported that the concentration of PCDD/Fs from small incinerators in Korea much higher than that from MSWIs. [1]

Table 1. PCDD/Fs measurment results in ambient air

Site	Summer	Fall	Winter
Incinerator area A	0.672	0.871	1.161
Industrial area B	NA	0.130	0.071
Industrial area C	NA	0.113	0.171

Relationships between sources and PCDD/Fs in air ;The MSWI of site A has been monitored for last two years.[1] The PCDD/Fs homologue patterns in stack gas sample and are presented in Figure 1. The patterns of samples are similar each other with domination by tetra, penta, hexa-chlorinated doxins and furans. These results indicat that PCDD/Fs emitted from incinerator may influence on the ambient air and as observed in the PCA analysis.

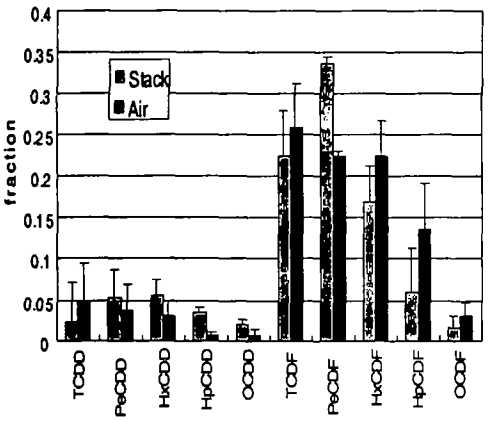


Figure 1. PCDD/Fs homologue patterns in stack gas and air samples in site A

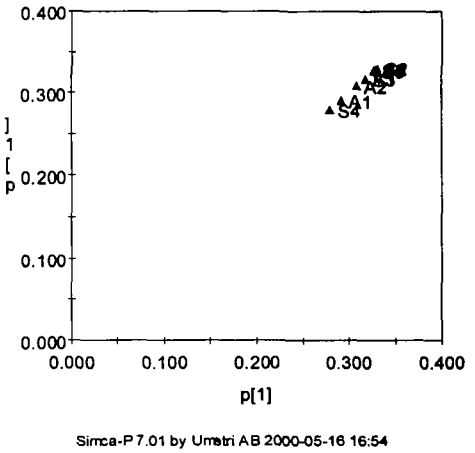
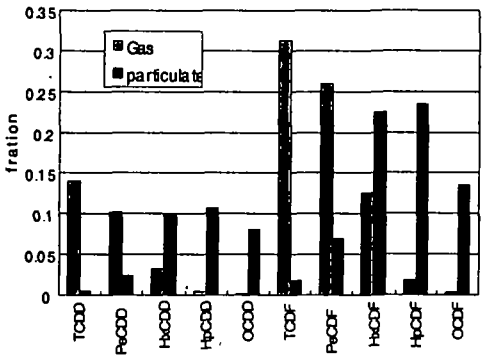
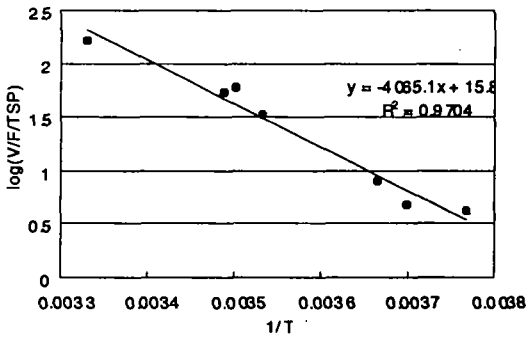


Figure 2. PCA analysis of stack gas and air samples

Gas/Particle partitioning of PCDD/Fs ; The measured PCDD/Fs data (particle bound and gaseous) are summarized in Table 2. As shown in Figure 3, a peculiar pattern of PCDD/Fs homologue is observed in each phase. Higher chlorinated PCDD/Fs in particle phase and lower chlorchlorinated PCDD/Fs in gas phase are dominant. These results are in accord with previous studies. [3,4,5] Log [(vapour)/(particle/TSP)] is related to 1/T and a good correlation (r=0.9704) is obtained but we could not find any significant relationships with other air conditions.

Figure 3. PCDD/Fs homologue patterns in two phases Figure 4. Plot of log{V/(F/TSP)} vs 1/T





References

1. J.E.Oh,K.T.Lee, J.W.Lee.,Y.S.Chang, Chemosphere, Vol 38, No 9, 2097-2108, 1999.
2. K.J.Shin, Y.S.Chang. Chemosphere, Vol38, No 11, 2655-2666, 1999.
3. B.D.Eitzer, R.A.Hites, ES&T, Vol 23, No 11, 1389-1395, 1989.
4. H.Yamasaki, K.Kuwata, H.Miyamoto, ES&T, Vol 23, No 16, 189-193, 1989
5.R.G.M.Lee, K.C.Jones, ES&T, Vol 33, No 33, 3596-3604, 1999

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Table 2. Concentration of PCDD/Fs isomers in air (pg/Nm^3)

	Site A (Incinerator area)						Site B(industrial area)				Site C(industrial area)			
isomer	Summer-F	Summer-P	fall-F	fall-P	winter-F	winter-P	fall-F	fall-P	winter-F	winter-P	fall-F	fall-P	winter-F	winter-P
2378-TCDD	0.004	0.018	0.028	0.009	0.027	0.003	0.001	0.004	0.002	0.001	0.002	0.001	0.003	0.002
12378-PeCDD	0.033	0.070	0.133	0.009	0.186	0.001	0.009	0.008	0.005	0.001	0.005	0.001	0.020	0.001
123478-HxCDD	0.086	0.017	0.181	0.002	0.111	0.000	0.018	0.003	0.003	0.001	0.003	0.001	0.015	0.000
123678-HxCDD	0.181	0.039	0.311	0.005	0.197	0.001	0.035	0.005	0.006	0.000	0.006	0.000	0.019	0.000
123789-HxCDD	0.088	0.012	0.252	0.002	0.127	0.001	0.028	0.002	0.004	0.000	0.004	0.000	0.017	0.000
1234678-HpCDD	1.089	0.047	1.753	0.004	1.150	0.004	0.287	0.012	0.049	0.001	0.049	0.001	0.141	0.001
OCDD	1.731	0.044	3.542	0.011	2.825	0.027	1.093	0.032	0.114	0.012	0.114	0.012	0.348	0.013
2378-TCDF	0.102	0.449	1.403	0.630	0.323	0.040	0.069	0.363	0.079	0.017	0.079	0.017	0.070	0.030
12378-PeCDF	0.119	0.363	0.475	0.079	0.293	0.030	0.051	0.178	0.041	0.009	0.041	0.009	0.066	0.020
23478-PeCDF	0.156	0.227	1.645	0.089	1.336	0.024	0.130	0.094	0.056	0.015	0.056	0.015	0.140	0.018
123478-HxCDF	0.447	0.231	1.068	0.027	0.593	0.023	0.123	0.051	0.040	0.011	0.040	0.011	0.139	0.018
123678-HxCDF	0.376	0.202	0.828	0.019	0.603	0.006	0.116	0.025	0.030	0.004	0.030	0.004	0.111	0.004
234678-HxCDF	0.166	0.020	0.082	0.000	0.758	0.004	0.020	0.002	0.040	0.002	0.040	0.002	0.160	0.002
123789-HxCDF	0.815	0.125	1.214	0.007	0.226	0.006	0.131	0.010	0.014	0.003	0.014	0.003	0.057	0.003
1234678-HpCDF	2.339	0.184	4.950	0.013	2.042	0.009	0.610	0.022	0.109	0.004	0.109	0.004	0.505	0.004
1234789-HpCDF	0.614	0.031	0.827	0.001	0.280	0.001	0.130	0.002	0.018	0.001	0.018	0.001	0.093	0.002
OCDF	2.915	0.058	5.007	0.004	1.716	0.003	0.544	0.005	0.144	0.002	0.144	0.002	0.861	0.003
TCDD	3.171	0.112	2.739	2.262	2.109	0.151	0.081	0.652	0.058	0.025	0.058	0.025	0.147	0.114
PeCDD	2.301	0.529	4.179	0.473	3.263	0.065	0.228	0.214	0.120	0.035	0.120	0.035	0.358	0.066
HxCDD	0.712	2.122	5.901	0.085	2.990	0.016	0.553	0.070	0.103	0.003	0.103	0.003	0.378	0.004
HpCDD	0.098	2.281	3.572	0.009	2.189	0.009	0.573	0.026	0.095	0.002	0.095	0.002	0.287	0.002
OCDD	0.044	1.731	3.542	0.011	2.825	0.027	1.093	0.032	0.114	0.012	0.114	0.012	0.348	0.013
TCDF	6.997	0.379	8.479	7.181	5.966	0.633	0.461	2.419	0.369	0.120	0.369	0.120	0.682	0.447
PeCDF	5.803	1.481	11.844	1.738	7.956	0.129	0.931	1.300	0.389	0.058	0.389	0.058	1.051	0.132
HxCDF	2.819	4.833	9.575	0.231	6.254	0.053	1.198	0.287	0.294	0.029	0.294	0.029	1.154	0.038
HpCDF	0.382	5.047	8.306	0.020	3.324	0.016	1.094	0.036	0.190	0.008	0.190	0.008	0.914	0.011
OCDF	0.058	2.915	5.007	0.004	1.716	0.003	0.544	0.005	0.144	0.002	0.144	0.002	0.861	0.003